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Differentiation between ferroelectricity and thermally stimulated current in pyrocurrent measurements of multiferroic $M\mathrm{Mn_7O_{12}}$ (M= Ca, Sr, Cd, Pb)

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This work investigated the electric polarization of $M\mathrm{Mn_7O_{12}}$ (M = Ca, Sr, Cd, Pb) by means of both the conventional pyroelectric current (PC) method and the bias electric field (BE) method. All samples generated intense, broad peaks below the highest magnetic ordering temperature (T_{N1}) during PC measurements. In contrast, these peaks were not observed in the BE data, indicating that they are not intrinsically generated through ferroelectricity but rather are thermally stimulated current (TSC) in origin. In addition to the TSC peaks, we observed anomalous small, sharp peaks in both the PC and BE data at T_{N2}, leading to a very small relative polarization value of $\Delta P \sim 0.2\ \mu\mathrm{C/m^2}$ at 46 K in the case of $\mathrm{CaMn_7O_{12}}$ and values of $\Delta P \sim 0.2\ \mu\mathrm{C/m^2}$ at 33 K for $\mathrm{CdMn_7O_{12}}$ and $\Delta P \sim 4.0\ \mu\mathrm{C/m^2}$ at 77 K for $\mathrm{PbMn_7O_{12}}$, while $\mathrm{SrMn_7O_{12}}$ showed no measurable polarization. In the case of $\mathrm{CaMn_7O_{12}}$, large ferroelectric polarization values below T_{N1} have been reported: 440 $\mu\mathrm{C/m^2}$ for a polycrystalline sample and 2870 $\mu\mathrm{C/m^2}$ for a single crystal. Nevertheless, we conclude from the present results that these reported large polarization values are not associated with intrinsic ferroelectricity in $\mathrm{CaMn_7O_{12}}$.

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I. INTRODUCTION

Over the last decade, since the discovery of the magnetic-field-induced electric polarization control phenomenon in rare-earth perovskites, magnetoelectric multiferroic materials have attracted much attention [1–3]. Because ferroelectric order is not a primary order parameter in such multiferroic compounds (known as spin-driven multiferroics), their ferroelectric polarization values are relatively small compared with those of conventional ferroelectric materials. However, with regard to practical applications, a large polarization value in conjunction with a high phase transition temperature is desirable, even in spin-driven multiferroics. There are several coupling mechanisms between spin orderings and ferroelectricity. The exchange striction mechanism, in which the electric dipole moment $\boldsymbol{p}$ is proportional to the symmetric exchange interaction $\boldsymbol{S}_i \cdot \boldsymbol{S}_j$, is the strongest coupling in spin-driven multiferroics. In fact, in some spin-driven multiferroics, relatively large ferroelectric polarization values, such as $\sim$1500 $\mu\mathrm{C/m^2}$ in orthorhombic $\mathrm{HoMnO_3}$ and 3600 $\mu\mathrm{C/m^2}$ in $\mathrm{GdMn_2O_5}$, have been induced through this mechanism [4–6]. Another potential coupling process is the inverse Dzyaloshinskii-Moriya (DM) mechanism [7–9], in which $\boldsymbol{p}$ is proportional to $\boldsymbol{S}_i \times \boldsymbol{S}_j$. This mechanism allows noncollinear spin systems, including cycloid and proper screw structures, to exhibit ferroelectricity. However, the polarization values induced by the inverse-DM effect are normally 1 order of magnitude smaller than those obtained via the exchange striction mechanism, such as $\sim$100 $\mu\mathrm{C/m^2}$ in $\mathrm{CuCrO_2}$ and $\sim$50 $\mu\mathrm{C/m^2}$ in $\mathrm{MnWO_4}$ [10–12].

Interestingly, in the case of $\mathrm{CaMn_7O_{12}}$, several groups have reported relatively large ferroelectric polarization, in spite of the noncollinear helical magnetic ordering in this material that leads to coupling through the inverse DM effect [13,14]. $\mathrm{CaMn_7O_{12}}$ is known to have two magnetic phase transitions, at $T_{\mathrm{N1}} = 90$ K and $T_{\mathrm{N2}} = 48$ K. Neutron diffraction experiments have shown that a helical magnetic structure with propagation vector $\boldsymbol{k} = (0,1,0.963)$ and a polar magnetic point group is stabilized in the range defined by $T_{\mathrm{N2}} \leqslant T \leqslant T_{\mathrm{N1}}$, although the complex magnetic structure with multi-k below T_{N2} has not yet been resolved [14–17]. Zhang *et al.* reported the first ever ferroelectric polarization obtained by pyroelectric current measurements of a polycrystalline sample, with a value of $\sim$440 $\mu\mathrm{C/m^2}$, appearing below $T_{\mathrm{N1}} = 90$ K [13]. Johnson *et al.* subsequently found a very large polarization value of 2870 $\mu\mathrm{C/m^2}$ during single-crystal pyroelectric studies [14]. Moreover, some theoretical work has reproduced this large ferroelectric polarization on the basis of model analysis and first-principles calculations [18–21]. In these theoretical papers, it has been argued that a combination of exchange striction and inverse DM mechanisms plays an important role in the emergence of significant polarization values for $\mathrm{CaMn_7O_{12}}$.

Recently, Glazkova *et al.* synthesized other $M\mathrm{Mn_7O_{12}}$ compounds with M = Sr, Cd, and Pb by high-pressure synthesis methods and reported their magnetic and dielectric properties based on magnetization, specific heat, and dielectric constant measurements [22–24]. The first two compounds were found to exhibit two magnetic transitions, at $T_{\mathrm{N1}} = 87$ K and $T_{\mathrm{N2}} = 63$ K in $\mathrm{SrMn_7O_{12}}$, and $T_{\mathrm{N1}} = 88$ K and $T_{\mathrm{N2}} = 33$ K in $\mathrm{CdMn_7O_{12}}$ [22]. In addition, $\mathrm{PbMn_7O_{12}}$ exhibited three magnetic phase transitions at $T_{\mathrm{N1}} = 83$ K, $T_{\mathrm{N2}} = 77$ K, and $T_{\mathrm{N3}} = 43$ K [23]. The authors also presented pyroelectric current results and reported that a large current flow was observed in the vicinity of T_{N1} in all the compounds, a phenomenon that has also been reported for $\mathrm{CaMn_7O_{12}}$ [13,14]. Although the authors suggested the

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possibility that this current is not caused by ferroelectricity but rather by a thermally stimulated current (TSC) [25–28], it was not possible to make a definitive conclusion due to the lack of a detailed investigation at that time. In some multiferroics, the TSC leads to a very large electric current flow during pyroelectric current (PC) measurements, and this has sometimes been misinterpreted as intrinsic PC leading to ferroelectricity [29–34]. Recently, however, Ngo *et al.* and De *et al.* have introduced several methods to distinguish TSC from intrinsic PC [35,36]. In the present work, we investigated the origin of the significant current observed during previous PC measurements of $M\mathrm{Mn_7O_{12}}$ (M = Ca, Sr, Cd, Pb), using both the conventional PC method and the bias electric field (BE) method.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of $M\mathrm{Mn_7O_{12}}$ (M = Ca, Sr, Cd, Pb) were prepared with high-pressure synthesis methods [22–24]. The quality of samples for $\mathrm{CdMn_7O_{12}}$ (sample 1) and the others, evaluated by x-ray powder diffraction, is given in the supporting information in Refs. [22] and [24], respectively. The oxygen content was not determined by chemical methods due to the presence of impurities that would give systematic shifts in the measured oxygen content. The samples were stoichiometric within the accuracy of structural refinements using synchrotron x-ray and neutron powder diffraction.

The sample pellets were hardened with disk-shaped, and silver paste was employed as electrodes. The electrodes had area S and thickness d values of $S = 11.0$ mm^2 and $d = 0.80$ mm for $\mathrm{CaMn_7O_{12}}$, $S = 23.7$ (4.6) mm^2 and $d = 1.52$ (0.50) mm for sample 1 (sample 2) for $\mathrm{SrMn_7O_{12}}$, $S = 10.0$ (16.6) mm^2 and $d = 0.96$ (0.65) mm for sample 1 (sample 2) for $\mathrm{CdMn_7O_{12}}$, and $S = 19.6$ mm^2 and $d = 1.15$ mm for $\mathrm{PbMn_7O_{12}}$. During the PC measurements of all samples, the electric current was measured in the absence of an electric field with warming after cooling from the poling temperature T_{pole} under an electric field E_{p} to 10 K. In the case of the BE method, we measured the electric current under a bias electric field E_{bias} with warming after cooling to 10 K in the absence of an electric field. A temperature sweep rate of 7.5 K/min was employed. During all measurements, a Keithley 6517B electrometer was employed.

III. RESULTS AND DISCUSSION

A. $\mathrm{CaMn_7O_{12}}$

Figure 1(a) shows the results obtained from PC measurements of $\mathrm{CaMn_7O_{12}}$. Here, an intense, broad peak is observed at 87 K, a value that is slightly lower than the magnetic phase

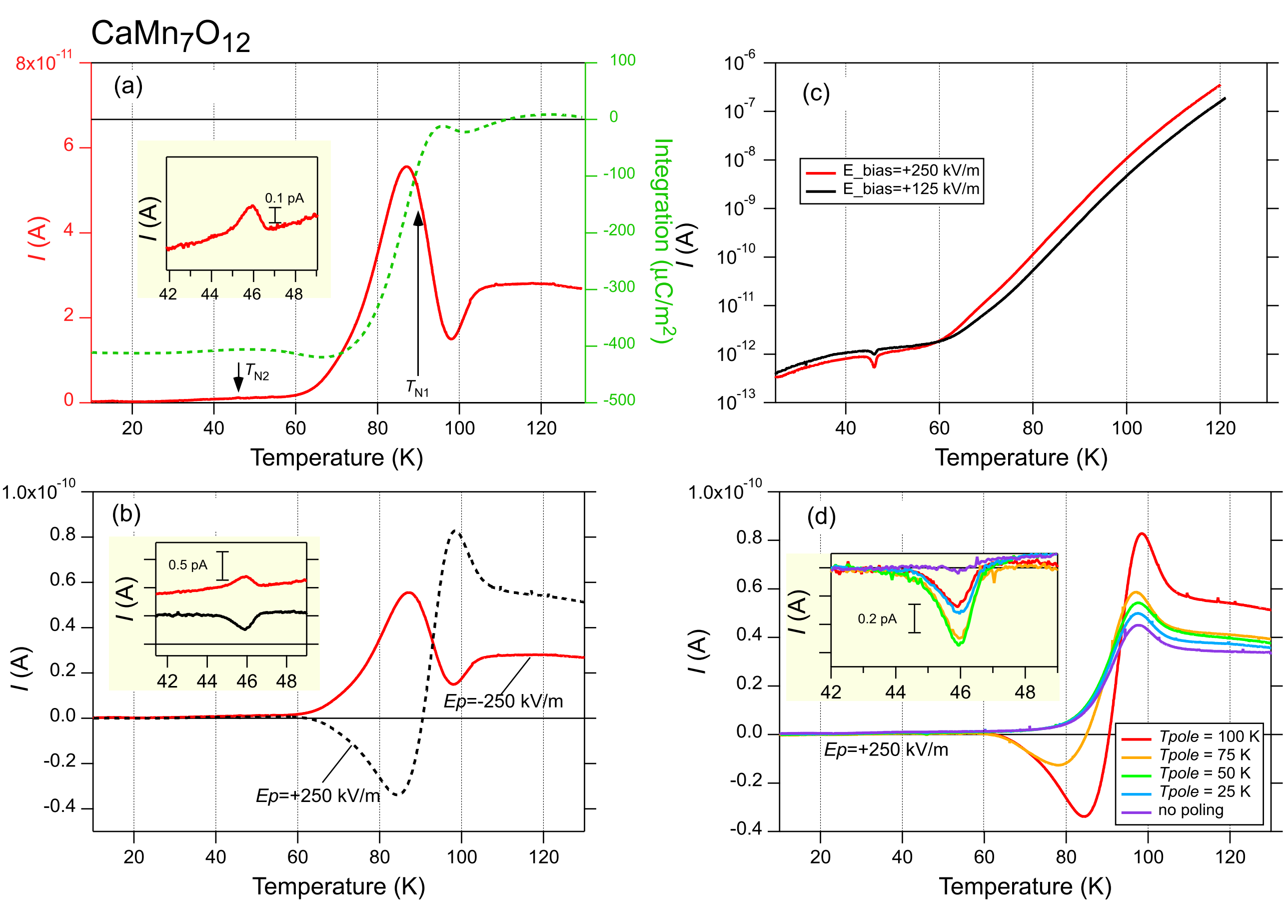

FIG. 1. Temperature dependence in the electric current with heating in $\mathrm{CaMn_7O_{12}}$. (a, b) Current was measured after cooling from $T_{\mathrm{pole}} = 100$ K to 10 K with an electric field. The dotted line in (a) shows the temperature dependence of the total electric charge, integrated as a function of time. (c) Variations in the electric current in $\mathrm{CaMn_7O_{12}}$ with heating under a bias electric field (E_{bias}). (d) Electric current in $\mathrm{CaMn_7O_{12}}$ with heating at several poling temperature conditions. The insets in (a, b, d) show magnification in the vicinity of 46 K.

transition temperature $T_{N1} = 90$ K. In previous PC measurements, this broad peak was also observed at a temperature of ~70 K, again lower than T_{N1} [13,14]. Integrating the measured current as a function of time, we obtained a total electric charge of ~400 $\mu C/m^2$ for polycrystalline $CaMn_7O_{12}$, as shown in Fig. 1(a). The integrated value obtained from the present measurements is consistent with the electric polarization value P previously reported for a polycrystalline sample of this material: ~440 $\mu C/m^2$ [13]. As shown in the inset to Fig. 1(a), a small but sharp peak was observed at 46 K, which is close to T_{N2}. The peaks observed at 87 K and 46 K were reversible upon switching the electric field, as shown in Fig. 1(b).

In some multiferroics, the TSC leads to significant electric current flow during PC measurements, which is sometimes misinterpreted as intrinsic PC associated with ferroelectricity [29–34]. When an electric field is applied at high temperature and the sample is cooled, electric charges are trapped on defects or impurity in the sample. Subsequently, the warming temperature gives rise to discharging the trapped electric charges, leading to observation of electric current as a TSC. Since the TSC is observed at temperatures far from the magnetic phase transition temperature in most cases, it can typically be easily distinguished from intrinsic PC. However, in the case of $CaMn_7O_{12}$, the temperature at which the current is observed is very close to the transition temperature, and we therefore used the BE method to distinguish TSC from intrinsic PC in this study, based on the work of De *et al.* [36]. The results are summarized in Fig. 1(c). The electric current peak seen in PC measurements should be generally observed even in data from the BE method if it does indeed originate from a ferroelectricity [36]. However, the large, broad peak at 87 K disappears under bias electric fields (E_{bias}), leaving only the small, sharp peaks around T_{N2}. Based on these results, we believe that the large peak in the vicinity of T_{N1}, leading to the pronounced electric polarization of $CaMn_7O_{12}$, is not caused by ferroelectricity but rather by the TSC. In addition, the small, sharp peak at T_{N2} is attributed to ferroelectricity.

The TSC can be assessed by measuring the PC after cooling from different poling temperatures (T_{pole}) [35]. As shown in Fig. 1(d), the temperature dependence of the electric current strongly depends on the value of T_{pole}. Poling from $T_{pole} = 100$ K gives rise to two negative peaks at 87 K (~T_{N1}) and 46 K (~T_{N2}), while a single positive peak is observed around 100 K. With decreasing T_{pole}, one negative peak at 87 K disappears at $T_{pole} = 50$ K. In general, the TSC is seen after poling from a temperature above which the TSC begins to discharge. In the case of $CaMn_7O_{12}$, the temperature at which discharge starts is ~65 K, which is consistent with the results showing that the large negative peak at 87 K disappears below 65 K. Conversely, the other negative peak at 46 K, corresponding to ferroelectricity, remains present even at $T_{pole} = 25$ K. One positive peak remains even for the case without poling, meaning that electric charges trapped in the sample are not completely discharged by the heating process.

B. $SrMn_7O_{12}$

$SrMn_7O_{12}$ exhibits two magnetic phase transitions at $T_{N1} = 87$ K and $T_{N2} = 63$ K [22]. As shown in Fig. 2(a), two broad peaks with opposite signs are observed at ~73 K and 89 K, and

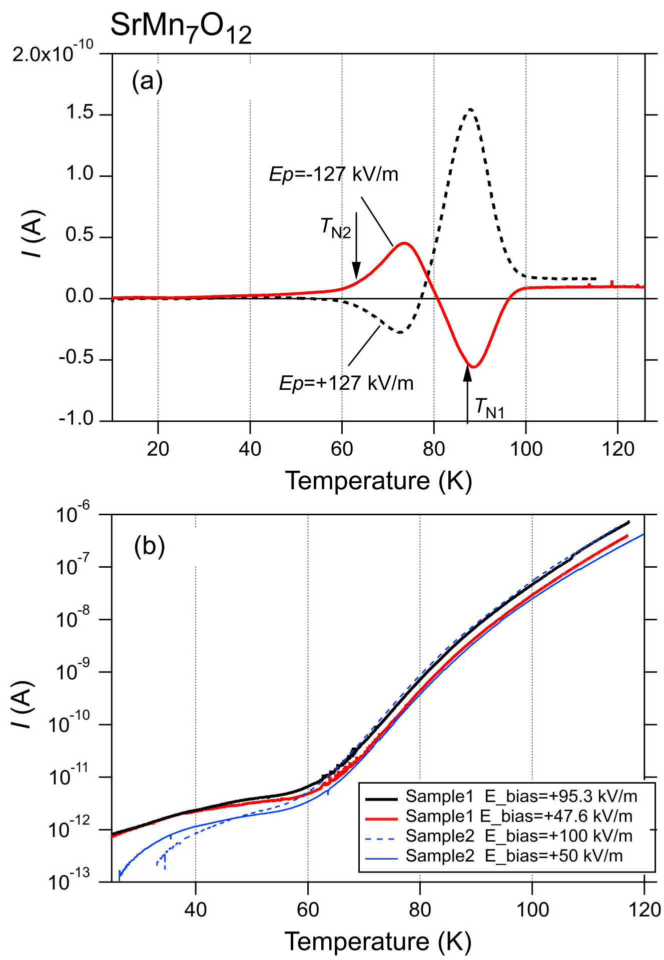

FIG. 2. (a) Variations in the electric current with heating for sample 1 of $SrMn_7O_{12}$ after cooling from $T_{pole} = 100$ K under poling electric fields of $E_p = -127$ kV/m (solid line) and $E_p = +127$ kV/m (dotted line). (b) Electric current with heating for samples 1 and 2 of $SrMn_7O_{12}$ under a bias electric field (E_{bias})

these are reversible upon switching E_p. However, these peak positions are not completely equivalent to the magnetic phase transition temperatures, suggesting that the broad peaks seen in PC measurements are not related to magnetic orderings. Moreover, the BE data for $SrMn_7O_{12}$ clearly show the disappearance of these broad peaks, as can be seen from Fig. 2(b). We can thus conclude that the broad peaks generated during the PC measurements of $SrMn_7O_{12}$ are not related to ferroelectricity. In addition, unlike $CaMn_7O_{12}$, the $SrMn_7O_{12}$ did not generate any sharp peaks around T_{N2}. Assuming that the expected PC peak at T_{N2} in $SrMn_7O_{12}$ is on the order of 0.1 pA, as observed for $CaMn_7O_{12}$, it could be obscured by the large TSC peak. To ascertain the variations in these phenomena between $SrMn_7O_{12}$ samples, we measured two samples synthesized independently. Both samples exhibited similar behaviors as assessed on a qualitative basis, with the exception of their conductivities in the low-temperature region.

C. $CdMn_7O_{12}$

Magnetic phase transitions have been reported at $T_{N1} = 88$ K and $T_{N2} = 33$ K in $CdMn_7O_{12}$ [22]. The observed

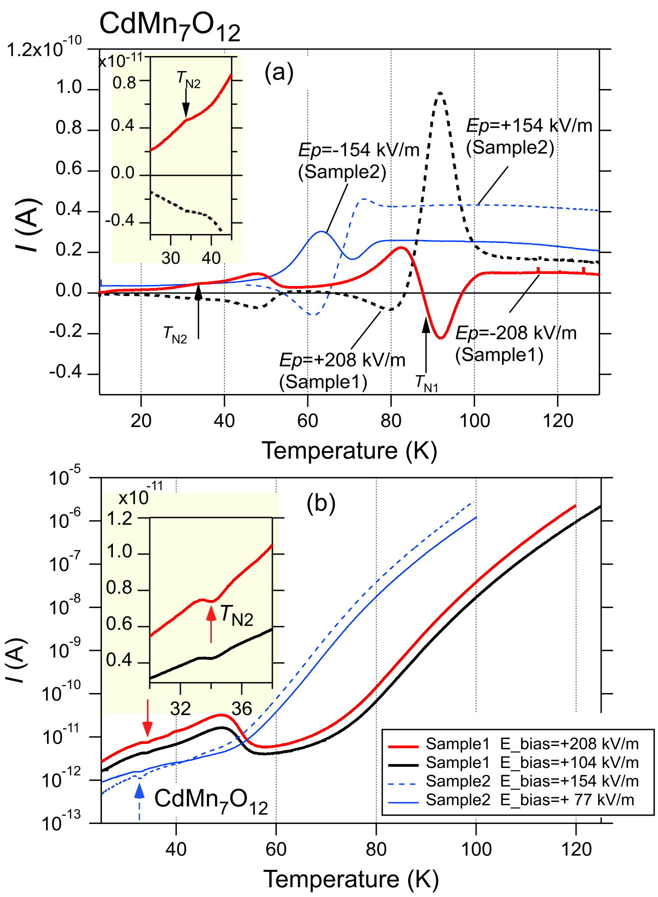

FIG. 3. (a) Variations in the electric currents of two samples of $CdMn_7O_{12}$ with heating. Currents were measured after cooling in an electric field of $E_p = +208$ (–208) kV/m for sample 1 and $E_p = +154$ (–154) kV/m for sample 2, from $T_{pole} = 100$ K to 10 K. (b) Electric currents of samples 1 and 2 of $CdMn_7O_{12}$ with heating under a bias electric field (E_{bias}). The insets in (a, b) show magnifications of the electric current around 33 K for sample 1.

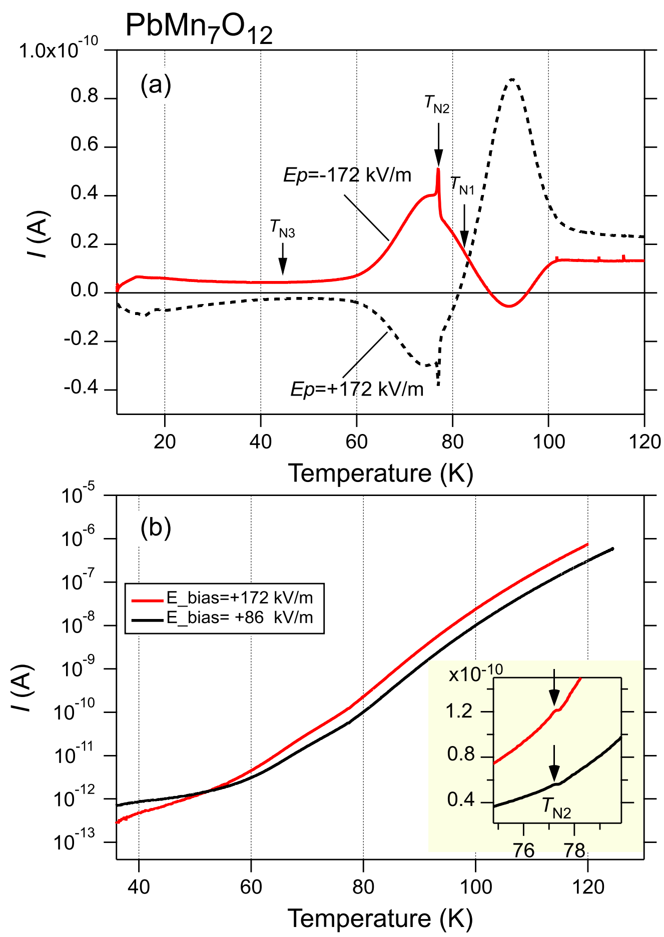

FIG. 4. (a) Variations in electric current with heating for $PbMn_7O_{12}$. The current was measured after cooling in an electric field of $E_p = +172$ (–172) kV/m from $T_{pole} = 100$ K to 10 K. (b) Electric current for $PbMn_7O_{12}$ with heating under a bias electric field (E_{bias}). The inset shows a magnification of the electric current in the vicinity of 77 K.

electric current during the PC measurements suggests a complicated structure and is highly dependent on the individual sample. As shown in Fig. 3(a), a single intense positive peak and two negative peaks were obtained at $E_p = +208$ kV/m in the case of sample 1, at ∼90 K, ∼80 K, and ∼50 K, respectively, and these were reversible upon switching E_p. These peak positions do not correspond to the magnetic phase transition temperatures, indicating that they are not related to magnetic orderings in $CdMn_7O_{12}$ and can be identified as originating from the TSC. The second sample (sample 2) generated peak positions that were completely different from those of sample 1, and these peaks are seen to disappear during the BE measurements, as shown in Fig. 3(b). The difference in results between samples is attributed to differences in conductivity, which is demonstrated by the BE data presented in Fig. 3(b).

Nevertheless, we observed a small signal in the vicinity of $T_{N2} = 33$ K for sample 1 of $CdMn_7O_{12}$, as can be seen in the inset to Fig. 3(a). This small anomalous peak was reproduced during the BE measurements [as seen in the inset to Fig. 3(b)], and so is believed to result from intrinsic PC related to magnetic/ferroelectric phase transitions in the $CdMn_7O_{12}$. In addition, sample 2, having a slightly different $T_{N2} = 31$ K (as identified by specific heat measurements), also generated a small peak during BE measurement at the same temperature, as indicated by the dotted line arrow in Fig. 3(b). As well, during BE measurements, sample 1 generated an anomalous broad hump in the vicinity of 50 K, while sample 2 did not. These results suggest that this anomaly was not intrinsic in origin but might be related to electric discharges from the electrode or to defects in sample 1. The presence of impurities in $CdMn_7O_{12}$ (sample 1) could be the origin of the broad hump [22].

D. $PbMn_7O_{12}$

Three magnetic phase transitions occurred at $T_{N1} = 83$ K, $T_{N2} = 77$ K, and $T_{N3} = 43$ K in $PbMn_7O_{12}$ [23], and the results of PC measurements are shown in Fig. 4(a). As observed with other MMn_7O_{12} compounds, large, broad peaks with opposite signs appeared at ∼75 K and ∼90 K. In addition, a sharp peak is evident at $T_{N2} = 77$ K in the $PbMn_7O_{12}$ data, and this is reversible upon switching E_p. When employing

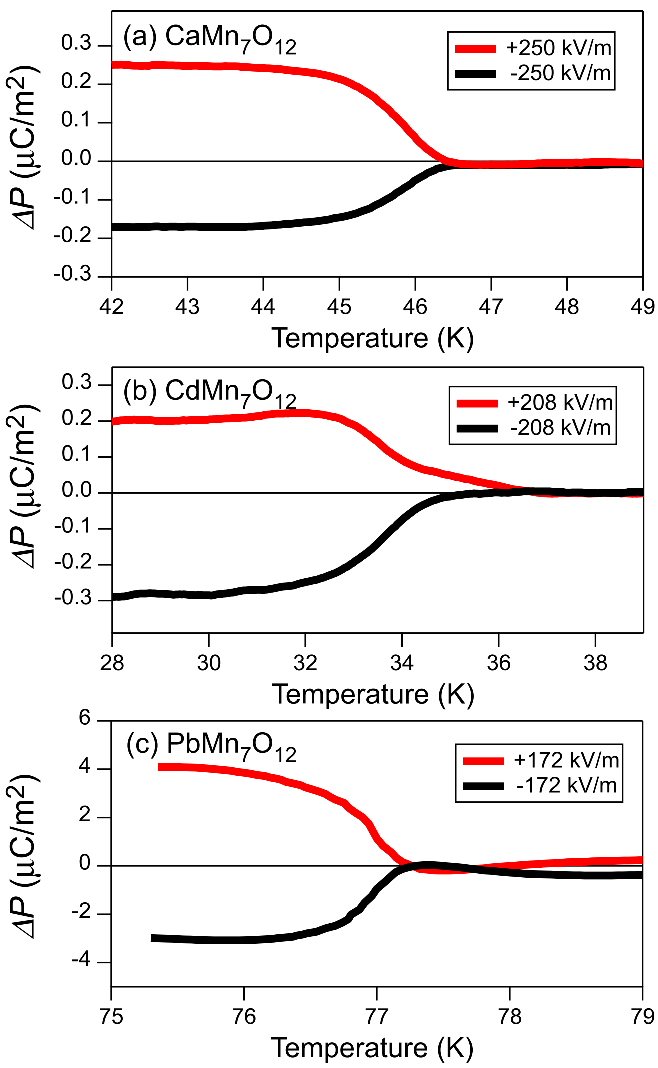

FIG. 5. Variations in the relative value of intrinsic electric polarization (ΔP) in (a) $CaMn_7O_{12}$, (b) $CdMn_7O_{12}$, and (c) $PbMn_7O_{12}$.

the BE method, only the sharp peak at 77 K was retained [as seen in the inset to Fig. 4(b)], while the large broad peaks disappeared, as demonstrated in Fig. 4(b). On the basis of these results, we can say that the sharp peak at T_{N2} generated by $PbMn_7O_{12}$ originates from intrinsic PC, which leads to ferroelectric polarization below T_{N2}, while the two broad peaks result from TSC.

IV. SUMMARY AND CONCLUSIONS

This work investigated the electric polarizations of $M Mn_7O_{12}$ (M = Ca, Sr, Cd, Pb) by means of conventional PC measurements and the BE method. We observed several large, broad peaks in the PC data, appearing below T_{N1} in the case of each sample, together with a small, sharp peak at T_{N2} in the $CaMn_7O_{12}$, $CdMn_7O_{12}$, and $PbMn_7O_{12}$ results. In order to distinguish TSC from intrinsic PC leading to ferroelectric polarization, we examined the BE data acquired for these compounds. The intense peaks observed in the PC measurements on all samples measured disappear when using the BE method, indicating that they are not intrinsic PC associated with ferroelectricity but rather originate from the TSC. In contrast, small, sharp peaks have been identified as resulting from a PC leading to a small ferroelectric polarization. The relative ferroelectric polarization values at T_{N2} are summarized in Fig. 5: $\Delta P \sim 0.2\ \mu C/m^2$ in $CaMn_7O_{12}$, $\Delta P \sim 0.2\ \mu C/m^2$ in $CdMn_7O_{12}$, and $\Delta P \sim 4.0\ \mu C/m^2$ in $PbMn_7O_{12}$. A measurable PC peak was not found at T_{N2} in $SrMn_7O_{12}$ within the limits of experimental resolution but might be obscured by the large TSC peak.

Finally, in the case of $CaMn_7O_{12}$, we note that large ferroelectric polarizations of 440 $\mu C/m^2$ (for a polycrystalline sample [13]) and 2870 $\mu C/m^2$ (for a single crystal [14]) below T_{N1} have been reported based on broad peaks observed in PC measurements. On the basis of the data from the present study, however, we conclude that the previously reported large polarization values were not caused by intrinsic ferroelectric polarization but instead by the TSC.

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